

INTERNATIONAL PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY SEARCH REPORT

(Article 36 and Rule 70 of the PCT)

File number of the applicant or attorney P02140WO/AVA

ADDITIONAL PROCEDURE See information on the forwarding of the
international preliminary search report
(PCT/IPEA/416 Form)

International file number: PCT/EP 03/07003

International application date (*day/month/year*): 7/01/2003

Priority date (*day/month/year*): 7/23/2002

International patent classification (IPC) or national classification and IPC
F25J3/02

Applicant

LINDE AKTIENGESELLSCHAFT et al.

1. This international preliminary search report was drawn up by the office responsible for the preliminary international examination and will be forwarded to the applicant according to Article 36.
2. This REPORT comprises a total of 5 pages including this cover sheet.
X In addition, ATTACHMENTS are attached to the report; in this case, these are pages with descriptions, claims and/or drawings, which were amended and upon

which this report is based, and/or pages with corrections made by this office (see Rule 70.16 and section 607 of the administration guidelines on the PCT).

These attachments comprise a total of 4 pages.

3. This report contains information on the following items:

- I. Basis of the office action
- V. Substantiated finding according to Rule 66.2 a) ii) with respect to novelty, inventive activity and industrial applicability; documentation and clarifications for supporting this finding.

Date of filing of the petition

1/27/2004

Date of the finishing of this report

9/21/2004

Name and mailing address of the office that is responsible for the international examination:

European Patent Office

D-80298 Munich

Tel. +49 89 2399-0, Tx: 523656 epmu d

Fax: +49 89 2399-4465

Authorized employee

Göritz, D.

Tel.: +49 89 2399-7934

INTERNATIONAL PRELIMINARY

EXAMINATION REPORT

International File Number PCT/EP 03/07003

I. Basis for the report

1. With respect to the **components** of the international application (*replacement pages, which the filing office submitted in response to the request according to Article 14, are considered "originally filed" within the context of this report and are not attached to it, since they do not contain any amendments (Rules 70.16 and 70.17)*):

Description, pages:

1, 4-8 in the originally filed version
2, 3 submitted on 3/25/2004 with a letter dated 3/23/2004

Claims, Nos.:

1-7 submitted on 3/25/2004 with a letter dated 3/23/2004

Drawings, Pages

1/2-2/2 in the originally filed version

V. Substantiated findings according to Article 35(2) with respect to novelty, inventive activity and industrial applicability; documentation and clarifications to support these findings

1. Findings

Novelty (N)	Yes: Claims 1-7
	No: Claims
Inventive activity (IS)	Yes: Claims 1-7
	No: Claims

Industrial applicability (IA)

Yes: Claims: 1-7

No: Claims:

2. Documentation and Clarifications:

See supplementary sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT --
SUPPLEMENTARY SHEET**

International File Number PCT/EP03/07003

Regarding Item V:

1. Reference is made to the following documents:

D1: CHIU, C-H: "LPG-RECOVERY PROCESSES FOR BASELOAD LNG PLANTS EXAMINED" OIL AND GAS JOURNAL, PENNWELL PUBLISHING CO., TULSA, U.S., November 24, 1997 (11/24/1997), pages 59-63,

D2: DE 100 27 903 A (LINDE AG) December 13, 2001

D3: US-A-4 150 962 (COLTON, JOHN W.) April 24, 1979

2. Document D1 discloses (the references in parentheses relate to Drawing 3 of this document):

A process for liquefying a hydrocarbon-rich flow with simultaneous recovery of a C₃/C₄-rich fraction, whereby the liquefaction of the hydrocarbon-rich flow is carried out in heat exchange for at least one refrigerant and/or mixed refrigerant flow (MHE1+2), and the hydrocarbon-rich flow that is to be liquefied, after precooling (C3), is subjected to a rectifying column, in which higher hydrocarbons are separated from the hydrocarbon-rich flow that is to be liquefied, and then is subjected to further cooling (MHE1) and liquefaction (MHE2), whereby a C₂+-rich fraction that is recovered in the subsequent cooling of the hydrocarbon-rich flow is fed to the rectifying column as a reflux liquid.

The subject of Claim 1 is therefore distinguished from the known process in that a C_4/C_5 -rich fraction (20, 35) is fed to the rectifying column as an additional reflux liquid, and in that the feed point of the C_4/C_5 -rich fraction (20, 35) lies above the feed point of C_{2+} -rich fraction (5), and a mass transfer zone (M) is provided between the feed point of C_4/C_5 -rich fraction (20, 35) and the feed point of C_{2+} -rich fraction (5).

The subject of **Claim 1** is therefore new (Article 33(2) of the PCT).

3. The object that is to be achieved with this invention can thus be considered to increase the C_3 yield in the recovered C_3/C_4 -rich fraction.

Publication D2 describes a similar process for recovering a C_{2+} -rich fraction in which a C_{2+} -rich reflux liquid and, in addition, at the top a $C_3/C_4/C_5$ -rich fraction are fed to the rectifying column to increase the C_{2+} yield, whereby the feed points are obviously separated by a mass transfer zone. However, in this process, the C_{2+} -rich reflux liquid is recovered before the rectifying column, and the hydrocarbon-rich flow is not liquefied after the rectifying column, thus creating a basically different process flow.

From D3, a process is disclosed in which a C_{4+} -rich reflux liquid is fed to the rectifying column. Completely lacking in this process, however, is the C_{2+} -rich reflux liquid that is fed in separately via a mass transfer zone below the C_{4+} -rich reflux.

Consequently, the combination of features contained in Claim 1 in this version is not evident from any documents mentioned in the search report, nor are they suggested by these documents. The solution that is proposed for this object in Claim 1 of this application is thus based on an inventive activity (Article 33(3) of the PCT).

4. **Claims 2 to 7** are formulated as dependent claims of Claim 1 and thus also meet the requirements of the PCT relative to novelty and inventive activity (Articles 33(2) and (3) of the PCT).

Replaced by
ART 34 AMDT

LNG Baseload Plants are normally operated with refrigeration circuits, which consist of hydrocarbon mixtures. These mixture circuits are more energy-efficient than expander circuits and allow corresponding relatively low energy consumption in the case of high liquefaction outputs from the Baseload Plants.

In these plants, the heavy hydrocarbons that are contained in the natural gas must be separated to produce the inventory of the mixture circuits, to cover losses during operation and because of product requirements.

This usually happens in that the hydrocarbon-rich flow that is to be liquefied is pre-cooled to a temperature of -10 to -25°C and then is fed to a rectifying column. By means of a suitable column configuration, the higher hydrocarbons – here, the C_{3+} -rich hydrocarbons as well as benzene are meant – are then separated from the flow to be liquefied in the rectifying column. At the top of the rectifying column, a C_2 -rich fraction is drawn off and subjected to further cooling as well as liquefaction. In this case, the C_{3+} -hydrocarbon fraction that is recovered at the bottom of the rectifying column is concentrated with higher hydrocarbons to the extent that the rectifying column is set to the desired heating value in the C_2 -rich top product.

The fraction that contains higher hydrocarbons and that is separated from the flow that is to be liquefied in the rectifying column is normally then separated into its components by rectification, whereby the latter are partially used as so-called Make-up Fractions - for example C_2H_6 or C_3H_8 – for the mixture circuit or circuits or are recovered as additional product flows and optionally are fed to a further processing.

The separation of the above-mentioned C_{3+} -rich fraction is performed with, for example, the following rectifying columns: demethanizer, de-ethanizer, depropanizer

and optionally debutanizer. These columns allow the production of the following fractions: methane, ethane and ethane make-up, propane and propane make-up, LPG (liquid gas) as well as a C_{5+} -fraction.

It is disadvantageous in the above-described process, however, that the yield of C_4 -hydrocarbons is comparatively low.

The object of this invention is to indicate a generic process that makes possible the recovery of a C_3/C_4 -rich fraction – the so-called LPG fraction – with as high a C_3 yield as possible.

To achieve this object, it is proposed that a C_4/C_5 -rich fraction be fed directly and/or indirectly to the rectifying column as an additional reflux liquid, whereby the feed point of the C_4/C_5 -rich fraction is at the top of the rectifying column or is identical to the feed point of the C_{2+} -rich fraction.

In this case, the term “indirectly fed” is defined as a process in which the C_4/C_5 -rich fraction that is fed to the rectifying column as an additional reflux liquid is admixed into another flow that is fed to the rectifying column.

According to the invention, two different fractions are now fed to the rectifying column as reflux liquids.

Moreover – corresponding to an advantageous embodiment of the process according to the invention – if the feed point of the C_4/C_5 -rich fraction is at the top of the rectifying column, a mass transfer zone is provided between the feed point of the C_4/C_5 -rich fraction and the feed point of the C_{2+} -rich fraction.

If the feed point of the C_4/C_5 -rich fraction and the feed point of the C_{2+} -rich fraction coincide, a mass transfer zone can be provided below the common feed point –

Claims

1. Process for liquefying a hydrocarbon-rich flow, in particular a flow of natural gas, with simultaneous recovery of a C_3/C_4 -rich fraction, whereby the liquefaction of the hydrocarbon-rich flow is carried out in heat exchange for at least one refrigerant and/or mixed refrigerant flow, and the hydrocarbon-rich flow that is to be liquefied, after precooling, is subjected to a rectifying column, in which higher hydrocarbons are separated from the hydrocarbon-rich flow that is to be liquefied, and then is subjected to further cooling and liquefaction, whereby a C_{2+} -rich fraction that is recovered in the subsequent cooling of the hydrocarbon-rich flow is fed to the rectifying column as reflux liquid, characterized in that a C_4/C_5 -rich fraction (20, 35) is fed directly and/or indirectly to rectifying column (T1) as an additional reflux liquid, whereby the feed point of the C_4/C_5 -rich fraction (20, 35) is located at the top of rectifying column (T1) or is identical to the feed point of the C_{2+} -rich fraction (5).
2. Process according to claim 1, whereby the feed point of the C_4/C_5 -rich fraction is at the top of the rectifying column, wherein between the feed point of the C_4/C_5 -rich fraction (20, 35) and the feed point of the C_{2+} -rich fraction (5), a mass transfer zone (M) is provided.
3. Process according to claim 1, whereby the feed point of the C_4/C_5 -rich fraction is identical to the feed point of the C_{2+} -fraction, wherein a mass transfer zone (M) is provided below the common feed point.

4. Process according to one of the preceding claims 1 to 3, in which the higher hydrocarbons that are recovered in the rectifying column are separated by rectification in several steps, whereby one of these steps comprises the feeding of higher hydrocarbons in a depropanizer (T2), wherein the C₄/C₅-rich fraction (20, 35) that is fed to rectifying column (T1) as an additional reflux liquid is recovered in a depropanizer side column (T3), which is fed to a C₄+-rich fraction (14) that is drawn off from depropanizer (T2).
5. Process according to one of the preceding claims 1 to 3, in which the higher hydrocarbons that are recovered in the rectifying column are separated by rectification in several steps, whereby one of these steps comprises the feeding of higher hydrocarbons in a debutanizer, wherein the C₄/C₅-rich fraction (20, 35) that is fed to rectifying column (T1) as an additional reflux liquid is recovered in the debutanizer.
6. Process according to one of the preceding claims 1 to 3, wherein the C₄/C₅-rich fraction (20, 35) that is fed to rectifying column (T1) as an additional reflux liquid is recovered in a side column (T4) of rectifying column (T1) by a C₄+-rich fraction (30) being fed to this side column (T4) from rectifying column (T1).
7. Process according to one of the preceding claims 1 to 6, wherein the C₄/C₅-rich fraction (20, 35) that is fed to rectifying column (T1) as an additional reflux liquid is cooled before the feeding thereof (E5, E7).

Replaced by
ART 34 AMDT

8. Process according to claim 7, wherein the C_4/C_5 -rich fraction (20, 35) that is fed to rectifying column (T1) as an additional reflux liquid is at least partially condensed in its cooling (E5, E7).
9. Process according to one of the preceding claims 1 to 8, wherein the benzene content of the C_4/C_5 -rich fraction (20, 35) that is fed to rectifying column (T1) as an additional reflux liquid is less than 500 ppm, preferably less than 300 ppm.